Crystal Structure of 2-Aminobenzo[*c*]cinnoline

Tuncer HÖKELEK*† and Emine KILIÇ**

*Hacettepe University, Department of Physics, 06800 Beytepe-Ankara, Turkey

**Ankara University, Department of Chemistry, 06100 Tandoğan-Ankara, Turkey

In the title compound, C₁₂H₉N₃, the two benzonoid rings are each planar, but slightly twisted with respect to each other with a dihedral angle of 1.79(6)°. Intermolecular N-H...N hydrogen bonds stabilize the crystal structure by causing the formation of a supramolecular architecture.

(Received August 25, 2005; Accepted November 25, 2005; Published on web February 27, 2006)

It is known that, amino-substituted aromatic heterocyclic compounds are very important intermediates in organic synthesis and industry. Aminobenzo[*c*]cinnolines are the starting materials for the manufacturing of dyes, colored polyamide fibers, charge-generating agents for electrophotographic photo-receptors and electrochromic polymers. In addition, benzo[*c*]cinnoline and some of its derivatives are known to have mutagenic, herbicidal, antirheumatic, carcinogenic and microbial activities.¹ On the other hand, the diazonium salt of 2-aminobenzo[*c*]cinnoline is found to be used to modify glassy carbon electrodes.²

The title molecule was prepared by the reduction of 2-nitrobenzo[*c*]cinnoline according to a literature method.³ It was

crystallized from an EtOH/H₂O mixture (m. p. 542 K).

The X-ray analysis results are given in Tables 1–4. The positions of the H atoms were located by a difference synthesis, and refined isotropically. The molecular structure of the title compound is shown in Fig. 2. The α , β and γ rings are each planar, and are almost coplanar in the benzo[*c*]cinnoline skeleton. The dihedral angles between their least-squares planes are $\alpha/\beta = 1.24(6)$, $\alpha/\gamma = 1.79(6)$ and $\beta/\gamma = 0.77(6)$ °, which show that the two benzonoid rings are slightly twisted with respect to each other. This twisting depends on the degree of the steric interaction between the H atoms at C1 and C10

Fig. 1 Chemical diagram.

Fig. 2 Molecular structure of the title compound with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table 1 Crystal and experimental data

Formula: C ₁₂ H ₉ N ₃
Formula weight: 195.22
Crystal system: orthorhombic
Space group: <i>P</i> 2 ₁ 2 ₁ 2 ₁ <i>Z</i> = 4
<i>a</i> = 4.5873(1) Å
<i>b</i> = 13.6991(3) Å
<i>c</i> = 15.2056(4) Å
<i>V</i> = 955.55(4) Å ³
<i>D</i> _x = 1.357 g/cm ³
μ (Cu <i>K</i> α) = 0.671 mm ⁻¹
<i>T</i> = 298 K
Crystal color: green
Crystal size: 0.20 × 0.15 × 0.10 mm
λ (Cu <i>K</i> α) = 1.54184 Å
<i>R</i> = 0.0347 <i>wR</i> = 0.0947
No. of reflections measured = 1156
No. of reflections used = 1152 [<i>I</i> > 2 σ (<i>I</i>)]
No. of parameters = 172
Goodness-of-fit = 1.110
(Δ / σ) _{max} = 0.000
($\Delta\rho$) _{max} = 0.189 e Å ⁻³
($\Delta\rho$) _{min} = -0.125 e Å ⁻³
2 θ _{max} = 148.5°
Measurements: Enraf-Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: SHELXS-97
Refinement: full matrix

CCDC 281896 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

† To whom correspondence should be addressed.
E-mail: merzifon@hacettepe.edu.tr

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	x	y	z	U_{eq}
C1	0.0719(5)	0.30578(14)	0.18818(12)	0.0457(4)
C2	0.2773(5)	0.31955(13)	0.12265(12)	0.0458(5)
C3	0.3917(5)	0.41434(15)	0.10821(13)	0.0525(5)
C4	0.3064(5)	0.49052(15)	0.15897(14)	0.0538(5)
N5	0.0247(5)	0.55745(12)	0.27617(13)	0.0593(5)
N6	-0.1589(5)	0.55004(13)	0.34039(12)	0.0600(5)
C7	-0.4802(5)	0.4576(2)	0.43095(15)	0.0627(6)
C8	-0.6128(6)	0.37240(19)	0.45260(15)	0.0658(6)
C9	-0.5578(6)	0.28736(17)	0.40512(16)	0.0612(6)
C10	-0.3647(5)	0.28809(15)	0.33619(14)	0.0532(5)
C11	-0.2236(5)	0.37468(13)	0.31202(12)	0.0461(4)
C12	-0.2832(5)	0.46025(14)	0.35965(13)	0.0510(5)
C13	0.0991(5)	0.47708(13)	0.22698(13)	0.0489(5)
C14	-0.0176(5)	0.38307(13)	0.24109(12)	0.0437(4)
N15	0.3633(5)	0.24238(14)	0.07092(12)	0.0564(5)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

Table 3 Bond distances (Å) and angles (°)

C1	C2	1.384(3)	C10	C11	1.400(3)
C2	C3	1.418(3)	C11	C12	1.405(3)
C2	N15	1.376(3)	C12	C7	1.412(3)
C3	C4	1.356(3)	C13	N5	1.374(2)
N5	N6	1.294(3)	C13	C4	1.417(3)
N6	C12	1.387(3)	C13	C14	1.411(3)
C7	C8	1.357(4)	C14	C1	1.392(3)
C8	C9	1.394(3)	C14	C11	1.439(3)
C9	C10	1.372(3)			
C2-C1-C14	120.88(18)	C10-C11-C12	118.79(18)		
C1-C2-N15	120.15(18)	C10-C11-C14	124.62(17)		
C3-C2-N15	120.60(19)	C12-C11-C14	116.59(17)		
C1-C2-C3	119.24(17)	N6-C12-C11	123.45(17)		
C2-C3-C4	120.66(19)	N6-C12-C7	116.60(19)		
C3-C4-C13	120.61(19)	C11-C12-C7	119.9(2)		
N6-N5-C13	120.66(18)	N5-C13-C14	123.65(19)		
N5-N6-C12	119.77(16)	N5-C13-C4	117.38(18)		
C8-C7-C12	119.7(2)	C14-C13-C4	118.96(17)		
C7-C8-C9	120.8(2)	C1-C14-C13	119.64(18)		
C8-C9-C10	120.4(2)	C1-C14-C11	124.50(17)		
C9-C10-C11	120.3(2)	C11-C14-C13	115.86(16)		

[H1...H10 = 2.18(3) Å]. This interaction generates enlarged C11-C14-C1 [124.50(17)°] and C14-C11-C10 [124.62(17)°] angles and smaller ones, C4-C13-N5 [117.38(18)°] and

Table 4 Hydrogen-bonding geometry (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
N15-H151...N6 ⁱ	0.97(2)	2.14(2)	3.105(3)	170(2)
N15-H152...N15 ⁱⁱ	0.94(3)	2.23(3)	3.155(3)	172(3)
C1-H1...N5 ⁱ	0.96(2)	2.559(19)	3.473(3)	158.8(18)

Symmetry codes: (i) $2 - x, -1/2 + y, 1/2 - z$, (ii) $1/2 + x, 1/2 - y, -z$.

C7-C12-N6 [116.60(19)°], at the opposite side of the benzo[c]cinnoline skeleton. As known, the degree of the steric interaction depends on the position of the bulky substituent and its electron-releasing or withdrawing properties. In 1-nitrobenzo[c]cinnoline⁴ and 2-pyrrolidino-benzo[c]cinnoline,⁵ for instance, the dihedral angles between the two benzonoid rings (α/γ) are 8.4(2)° and 1.32(6)°.

The intermolecular N-H...N and C1-H...N hydrogen bonds (Table 4) stabilize the crystal structure, forming a supramolecular architecture, parallel to the *b*-axis.

Acknowledgements

The authors wish to acknowledge financial support of this work under a grant from Ankara University Scientific Research Fund (grant number: 20030705084).

References

1. E. Kılıç and S. Aktan, *Commun. Fac. Sci. Univ. Ank. Series B*, **2001**, 47, 37.
2. A. A. İsbir, A. O. Solak, Z. Üstündağ, S. Bilge, A. Natsagdorj, E. Kılıç, and Z. Kılıç, *Anal. Chim. Acta*, **2005**, 547, 59.
3. J. W. Barton and M. A. Cocket, *J. Chem. Soc.*, **1962**, 2454.
4. T. Hökelek, E. Kılıç, and S. Aktan, *Acta Cryst.*, **1999**, C55, 383.
5. T. Hökelek, E. Kılıç, and C. Tüzün, *Acta Cryst.*, **1991**, C47, 373.